

THE ROLE OF MODEL COMPOUND STUDIES IN COAL RESEARCH

A. C. Buchanan, III and Phillip F. Britt
Chemical and Analytical Sciences Division
Oak Ridge National Laboratory
P. O. Box 2008
Oak Ridge, Tennessee 37831-6197

Keywords: Model compounds, retrogressive, interfaces, hydrogen transfer

INTRODUCTION

The extraordinarily complex chemical and physical structure of coals continues to present coal scientists with major challenges in advancing the base of scientific knowledge required for the development of substantially improved coal utilization technologies. As a consequence, model compound studies play a foundational role in advancing coal science. Model compounds are employed in studies for: (a) determination of kinetic and mechanistic information relevant to coal pyrolysis and liquefaction chemistry, and to computational modeling of these processes; (b) development of new catalysts for coal conversion or upgrading of coal-derived liquids; (c) development and benchmarking of various spectroscopic methods for analysis of coal structure and constitution by NMR, FTIR, mass spectrometry, X-ray techniques (XPS, XANES), etc.; and, (d) exploration and development of new chemical reactions for coal such as depolymerization under mild conditions, selective heteroatom removal, etc.

The choice of a model compound should not be prescribed, and the rationale for the selection can vary with the goal of the research. In general, compounds are selected as substructures, or surrogates for a range of related substructures, in coal. The goal of these studies is to understand the behavior of a well-defined chemical system. Once a system is precisely understood then complexities found in coal can be added systematically, such as restricted mass transport, functional group interactions, medium and interfacial effects, etc. Whereas most early studies of model compounds involved simple molecular systems in homogeneous phases, current model compound studies include a substantial contribution from more complicated systems such as reporter molecules in multiphase media under coal conversion conditions¹, chemically and isotopically labeled coal derivatives², silica-immobilized organics³⁻⁵, and polymers⁶⁻⁹.

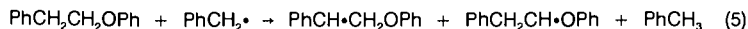
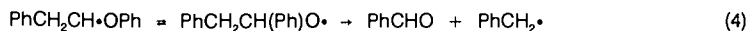
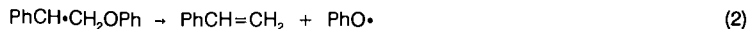
The breadth of use of model compounds in coal research precludes a thorough examination in this report. Instead, we will focus on the use of model compound studies to reveal kinetic and mechanistic details underlying coal pyrolysis and liquefaction. We will limit our examination of this topic to the presentation of four areas that we feel are prominent in current research, and that will continue to be significant in the near future. The aim is to illustrate where model compound studies can and do contribute to coal research, along with the presentation of an occasional brief example. The topics are arbitrarily categorized and, clearly, there exists a substantial degree of overlap among them.

Model Compounds Containing Heteroatoms

There has been substantial progress in obtaining detailed knowledge of the thermal chemistry of hydrocarbon models including aromatics, alkylaromatics, α,ω -diarylalkanes, and hydroaromatics, which has recently been reviewed by Poutsma¹⁰⁻¹¹ and Stein¹². The depth of our understanding for molecules containing heteroatoms (O, S, N) is not as advanced (for example, PhSCH_2Ph vs. the well-understood $\text{PhCH}_2\text{CH}_2\text{Ph}$)¹¹. Recent mass spectrometry studies by Winans and coworkers have demonstrated the abundance of heteroatom-containing molecules in coals, macerals, and extracts.¹³ For example, it is well-known that oxygen functionalities are particularly abundant in low rank coals and lignites. Furthermore, oxygen-containing functional groups have been implicated in the difficulty found in processing low rank coals.¹⁴ A more detailed understanding of the chemistry of oxygen-containing model compounds is needed.

We have recently reinvestigated the thermolysis of phenethyl phenyl ether ($\text{PhCH}_2\text{CH}_2\text{OPh}$, PPE),¹⁵ which is the simplest model for the β -aryl ether units that are

key constituents of lignin and which are also present in low-rank coals. This research has revealed a previously undetected reaction pathway that accounts for ca. 25% of the conversion of PPE, and which may account for some of the products previously observed in the pyrolyses of lignins. The standard chain propagation steps for free radical decomposition of PPE (Eqs. 1 & 2) must now be augmented by the chain propagation steps shown in Eqs. 3-5, which includes a step involving a neophyl-like rearrangement for an aliphatic radical α to oxygen prior to β -scission (Eq. 4).



We are in the process of examining substituent effects (relevant to lignin substructures) on the thermolysis of PPE. Our initial findings indicate that the additional reaction pathway is general, but that the selectivity for this pathway (and the rate of decomposition of PPE) is sensitive to the substitution pattern.

This research also revealed a general need for better defined rate constants and Arrhenius parameters for many of the individual reaction steps, which are important in unraveling reaction mechanisms, global reaction kinetics, and substituent effects for complex reactions. This data can be very difficult to extract from complex reactions such as observed for PPE, particularly when secondary reactions become important at low conversions. Franz and coworkers, for example, have been able to design experiments to directly measure such absolute rate data for the β -scission of $\text{PhCH}\cdot\text{CH}(\text{CH}_3)\text{OPh}$ ¹⁶, which provides key information relevant to Eq. 2 above. A particularly visible gap in our knowledge is the lack of absolute rate constants and Arrhenius parameters for hydrogen abstractions by phenoxy (and other aryloxy) radicals. Given the apparent importance of such reaction steps in the processing of lignins and low rank coals, kinetic information of this type would be very valuable.

The effect of a heteroatom substituent on a thermolysis reaction is not always easy to predict, and the results can range from subtle to dramatic. For example, we have found that pyrolysis of *p*-Me₃SiOPh(CH₂)₃Ph proceeds similarly to Ph(CH₂)₃Ph with little influence of the oxygen substituent on the reaction.⁴ Similarly, *m*-HOPhCH₂Ph is stable at 400°C as is the unsubstituted analog, PhCH₂Ph.¹⁷ On the other hand, McMillen and coworkers have shown that *o*- and *p*-HOPhCH₂Ph decay readily at 400°C, because an initial enol-keto tautomerization generates an intermediate with a thermally labile bond.¹⁷ The presence of the ortho-hydroxy group in guaiacol (*o*-HOPhCH₃) has been shown to decrease the O-C bond dissociation energy of the methoxy group by 7 kcal/mol, suggesting that hydrogen bonding interactions are important in the radical formed.¹⁸ Finally, thermolysis of 1-naphthol has been shown to proceed by C-C ring coupling prior to condensation (loss of water),¹⁹ while 1,3-dihydroxynaphthalene undergoes condensation first.²⁰ These few selected examples illustrate that there is much work to be done to understand the impact of oxygen in thermal reaction chemistry related to coal conversion, and a similar status exists for sulfur- and nitrogen-containing organic structures.

Retrogressive Reaction Pathways

The majority of previous model compound studies have been designed to learn about the cleavage of bonds during coal pyrolysis and liquefaction, and ways of altering reaction media and conditions to promote these reactions. There is now considerable interest in learning more about bond forming reactions and the conditions where they become kinetically competitive. Of particular interest are processes that form more refractory bonds since these reactions are the essence of retrogressive chemistry in coal processing. Malhotra and McMillen have discussed this chemistry with respect to hydrogen transfer reactions in a recent review.²¹

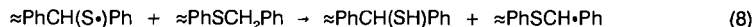
A current topic is the retrogressive chemistry that is prominent in the processing of low rank coals. This chemistry has been documented most completely by Solomon,

Serio, and coworkers who have proposed that the formation of new crosslinks in the coal network is associated with the loss of CO₂ and water from oxygen-containing functional groups. A recent review of this pyrolysis research has been published.²² These authors have also obtained substantial information recently on the effects of demineralization, aqueous pretreatments, introduction of ion-exchanged catalysts, etc. on the liquefaction behavior of low rank coals, techniques which are designed to reduce retrogressive reactions.²³ However, a clear definition of the actual chemical reactions underlying these processes remains elusive. Ring coupling following decarboxylation of acids has been presumed to be involved. However, there is surprisingly little relevant information available in the literature on such reactions, and McMillen and coworkers have recently shown that, under liquefaction conditions, decarboxylation of model aromatic carboxylic acids is not accompanied by significant ring coupling.²⁴ Hence, if CO₂ evolution is a signature of the cross-linking event, additional studies are required to determine the nature of the cross-linking reactions associated with decarboxylation. We have recently initiated a project to prepare polymeric model systems containing carboxylic acids to examine the impact of a polymeric network on the thermolysis chemistry.²⁵ The diffusional constraints imposed by such a polymer system may alter the reactivity pattern for the decarboxylation process, as we have occasionally observed previously in the pyrolysis pathways for silica-immobilized model compounds.

There are other types of retrogressive reactions that may be involved in coal processing that need to be studied in more detail. These include ring growth through a sequence of cyclization and aromatization, and radical recombinations and skeletal rearrangements that form strong bonds.²¹ We have found that restricted mass transport (induced by immobilization on silica) promotes retrogressive reactions for bibenzyl by both skeletal rearrangement (to PhCH(CH₃)Ph) and ring growth (to phenanthrene).³ We recently found that a similar rearrangement process appears to occur at 300°C for the structurally related silica-immobilized phenyl benzyl sulfide (≈PhSCH₂Ph), which accounts for 10-15% of the reaction. This process converts a



very labile linkage into a much more refractory diphenylmethane-type linkage. Our current hypothesis is that Eqs. 7-8 are the key chain propagation steps in this



process analogous to bibenzyl. The sulfur to carbon neophyl-like rearrangement for the fluid-phase analog of Eq. 7 has recently been directly observed by Alnajjar and Franz.²⁶ Coal science would benefit from an improved molecular level understanding of retrogressive reaction types, and the impact that coal physical properties and coal processing media may have on them.

Interfacial Chemistry

Coal is of course not a homogeneous material. It is a complex, heterogeneous solid that includes interdispersed mineral matter. Yet knowledge of organic-mineral matter interactions, and how they effect the reactivity of coal is only rudimentary. There is also growing evidence that water can play a significant role in affecting the course of chemical reactions during coal processing, which needs to be investigated in more detail.²³ A more complete description of coal reactivity under pyrolysis or liquefaction conditions requires a better molecular level understanding of the effect of minerals on coal reactivity in the solid state. Clays such as montmorillonite, for example, are known to be effective catalysts for organic reactions. They have also been proposed as key catalysts for the thermal alteration of lignin during the coalification process.²⁷ This suggests that catalytic interactions at the solid-solid interface are important. Recently, we were able to demonstrate that montmorillonite, and other small particle size silica-aluminas, can induce acid-catalyzed reactions in the solid state for several silica-immobilized model compounds including phenethyl phenyl ether.²⁸

The catalytic liquefaction of coal constitutes a truly multiphase system, involving solid coal and catalyst, hydrogen gas, and a hydrogen donor "solvent", where interfacial interactions are obviously important. Recently Malhotra and McMillen have

summarized the potential role of the reaction medium in transferring hydrogen atom activity from the catalyst to the coal reactive site.²¹ A very active area of research on coal conversion is the search for new nanoscale dispersed catalysts, which could improve the direct interaction of solid coal particles with catalyst.²⁹ Only recently has evidence begun to emerge that such solid state interactions might be important in affecting the outcome of coal conversion. For example, Bockrath and coworkers used a pulse-flow microreactor to show that organic hydrogen in coal can be exchanged with D₂ gas at low temperatures as a result of MoS₂ catalyst-coal interactions.³⁰ In collaboration with Snape and coworkers, we have made a preliminary investigation of the catalyzed hydrocracking of silica-immobilized diphenylmethane in the solid state using temperature programmed reduction (TPR) under high pressures of hydrogen with mass spectrometric detection of volatile products.³¹ We gained evidence, from the substantially lowered temperatures for benzene and toluene evolution, that a dispersed sulfided Mo catalyst can significantly promote the hydrogenolysis reaction (Eq. 9) in the solid state. The degree to which coal conversion can be modified

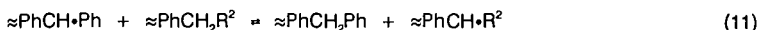
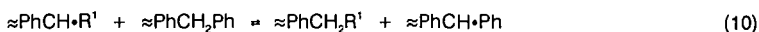


by dispersed catalysts, and the factors controlling such interactions, have only begun to be explored and are a frontier area for model compound research.

Hydrogen Transfer Chemistry

Despite the longstanding interest and the wealth of information available, improved knowledge of the mechanisms of hydrogen transfer remains a crucial area for the attention of model compound researchers. Hydrogen transfer reactions are important in both bond breaking and bond forming reactions. Of particular current interest are medium effects (solvent systems, catalysts, restricted mass transport, etc.) on hydrogen transfer processes. An array of hydrogen transfer steps have been invoked as being involved including hydrogen abstraction by radicals, transfer of free hydrogen atoms, reverse radical disproportionation (RRD), and radical hydrogen transfer (RHT). RHT involves hydrogen transfer from a cyclohexadienyl-type carrier radical to a substrate in a single step, and has gained significant attention in recent coal and model compound studies.^{21,32} However, contrary opinions on the importance of RHT have been recently presented.³³ The exact details aside, it appears that the presence of polycyclic aromatic hydrocarbons in solvent systems can mediate hydrogenolysis activity in coal liquefaction. Given the importance of controlling hydrogen utilization in the development of economically competitive coal utilization technologies, additional model compound research in this area is needed.

We have been actively investigating the effects of restricted mass transport, which may be important in coal chemistry, on thermolysis reactions through the study of silica-immobilized model compounds.³⁵ By employing two-component surfaces, one can begin to explore the effects of diffusionally constrained environments on hydrogen transfer processes. We have acquired evidence that a mechanism involving rapid serial hydrogen transfer steps on the surface can provide an alternative, non diffusional pathway for free-radical centers to "migrate" as illustrated below.³⁴



Moreover, we have recently found that the retrogressive radical chain rearrangement path for silica-immobilized bibenzyl (analogous to Eqs. 7-8 above) is more effectively inhibited by naphthalene spacers (hydrogen transfer barricades) than by hydrogen donor spacers such as tetralin (radical relay centers).³⁵ These results have important implications for the transfer of reactive sites in the cross-linked network structure of coal which must be explored in more detail.

Summary

Model compound studies have made and continue to make important contributions in advancing coal science, ranging from determination of quantitative kinetic information for elementary reaction steps to unravelling the effects of restricted diffusion or interfacial phenomena on chemical processes. Constant interactions between model compound and coal researchers will enhance the prospects that the model compound

researcher is performing work of relevance to coal science, and that the coal researcher is employing the appropriate scientific basis in interpretation of coal results. Research that reveals new information on the chemical reactions associated with heteroatom-containing model compounds, retrogressive reaction pathways, organic-mineral interactions and other interfacial effects, and details of hydrogen transfer processes is of particular current interest.

Acknowledgement

This research was sponsored by the Division of Chemical Sciences, Office of Basic Energy Sciences, U.S. Department of Energy, under Contract DE-AC05-84OR21400 with Martin Marietta Energy Systems, Inc.

References

1. Bockrath, B. C.; Schroeder, K. T.; Smith, M. R. *Energy and Fuels* **1989**, *3*, 268.
2. Stock, L. M. *Acc. Chem. Res.* **1989**, *22*, 427.
3. Buchanan, III, A. C.; Dunstan, T. D. J.; Douglas, E. C.; Poutsma, M. L. *J. Am. Chem. Soc.* **1986**, *108*, 7703.
4. Buchanan, III, A. C.; Biggs, C. A. *J. Org. Chem.* **1989**, *54*, 517.
5. Britt, P. F.; Buchanan, III, A. C. *J. Org. Chem.* **1991**, *56*, 6132.
6. Malhotra, R.; McMillen, D. F.; Tse, D. S.; St. John, G. A. *Energy Fuels* **1989**, *3*, 465.
7. McMillen, D. F.; Satyam, A.; Malhotra, R. *Proc., 7th Int. Conf. Coal Sci., Banff, Alberta, Canada, 1993*, Vol. II, 163.
8. Squire, K. R.; Solomon, P. R.; Carangelo, R. M.; DiTaranto, M. B. *Fuel* **1986**, *65*, 833.
9. Winans, R. E.; Hayatsu, R.; Squires, T. G.; Carrado, K. A.; Botto, R. E. *Prepr. Pap.-Am. Chem. Soc., Div. Fuel Chem.* **1990**, *35(2)*, 423.
10. Poutsma, M. L. *Energy Fuels* **1990**, *4*, 113.
11. Poutsma, M. L. "A Review of Thermolysis Studies of Model Compounds Relevant to Processing of Coal," Oak Ridge National Laboratory, ORNL/TM-10637, November, 1987.
12. Stein, S. E. *Acc. Chem. Res.* **1991**, *24*, 350.
13. Winans, R. E. "Mass Spectrometric Studies of Coals and Coal Macerals," In *Advances in Coal Spectroscopy*, Muezzelaar, H. L. C., Ed.; Plenum Press: New York, **1992**, 255.
14. Solomon, P. R.; Serio, M. A.; Despande, G. V.; Kroo, E. *Energy Fuels* **1990**, *4*, 42.
15. Britt, P. F.; Buchanan, III, A. C.; Hitsman, V. M. *Proc., 6th Int. Conf. Coal Sci., Newcastle-upon-Tyne, United Kingdom, 1991*, 207.
16. Autrey, S. T.; Alnajjar, M. S.; Nelson, D. A.; Franz, J. A. *J. Org. Chem.* **1991**, *56*, 2197.
17. McMillen, D. F.; Ogier, W. C.; Ross, D. S. *J. Org. Chem.* **1981**, *46*, 3322.
18. Suryan, M. M.; Kafafi, S. A.; Stein, S. E. *J. Am. Chem. Soc.* **1989**, *111*, 1423.
19. Poutsma, M. L.; Dyer, C. W. *J. Org. Chem.* **1982**, *47*, 3367.
20. McMillen, D. F.; Chang, S. -J.; Nigenda, S. E.; Malhotra, R. *Prepr. Pap.-Am. Chem. Soc., Div. Fuel Chem.* **1985**, *30(4)*, 414.
21. Malhotra, R.; McMillen, D. F. *Energy Fuels* **1993**, *7*, 227.
22. Solomon, P. R.; Fletcher, T. H.; Pugmire, R. J. *Fuel* **1993**, *72*, 587.
23. Serio, M. A.; Kroo, E.; Charpenay, S.; Solomon, P. R. *Prepr. Pap.-Am. Chem. Soc., Div. Fuel Chem.* **1993**, *38(3)*, 1021.
24. Manion, J. A.; McMillen, D. F.; Malhotra, R. *Prepr. Pap.-Am. Chem. Soc., Div. Fuel Chem.* **1992**, *37(4)*, 1720.
25. Britt, P. F.; Buchanan, III, A. C. *Proc., 7th Int. Conf. Coal Sci., Banff, Alberta, Canada, 1993*, Vol. II, 297.
26. Alnajjar, M. S.; Franz, J. A. *J. Am. Chem. Soc.* **1992**, *114*, 1052.
27. Hayatsu, R.; McBeth, R. L.; Scott, R. G.; Botto, R. E.; Winans, R. E. *Org. Geochem.* **1984**, *6*, 463.
28. Buchanan, III, A. C.; Britt, P. F.; Thomas, K. B.; Biggs, C. A. *Energy Fuels* **1993**, *7*, 373.
29. Derbyshire, F. J. *Energy Fuels* **1989**, *3*, 273.
30. Bockrath, B. C.; Finseth, D. H.; Hough, M. R. *Fuel* **1992**, *71*, 767.
31. Mitchell, S. C.; Lafferty, C. J.; Garcia, R.; Snape, C. E.; Buchanan, III, A. C.; Britt, P. F.; Klavetter, E. *Energy Fuels* **1993**, *7*, 331.
32. Smith, C. M.; Savage, P. E. *Energy Fuels* **1992**, *6*, 195.
33. Autrey, S. T.; Camaioni, D. M.; Ferris, K. F.; Franz, J. A. *Proc., 7th Int. Conf. Coal Sci., Banff, Alberta, Canada, 1993*, Vol. I, 336.
34. Buchanan, III, A. C.; Britt, P. F.; Biggs, C. A. *Energy Fuels* **1990**, *4*, 415.
35. Buchanan, III, A. C.; Britt, P. F.; Thomas, K. B. *Proc., 7th Int. Conf. Coal Sci., Banff, Alberta, Canada, 1993*, Vol. I, 627.